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Paramagnetism of $Cu_3RE_2W_4O_{18}$ Semiconductors (RE = Gd, Dy–Er)

T. Groń[a], E. Tomaszewicz[b], H. Duda[a] and S. Mazur[c]

[a]University of Silesia, Institute of Physics, Uniwersytecka 4, 40-007 Katowice, Poland

[b]West Pomeranian University of Technology, Department of Inorganic and Analytical Chemistry al. Piastów 42, 71-065 Szczecin, Poland

[c]International Laboratory of High Magnetic Fields and Low Temperatures, Gajowicka 95, 53-529 Wrocław, Poland

$Cu_3RE_2W_4O_{18}$ tungstates (RE = Gd, Dy–Er) are paramagnets in the temperature range 4.2–300 K visible also in the absence of the energy losses in the curve of the imaginary part of magnetic susceptibility, χ''. The negative values of the paramagnetic Curie–Weiss temperature, θ, may suggest the weak antiferromagnetic coupling below 4.2 K. The temperature independent component of magnetic susceptibility has a positive value indicating a domination of the Van Vleck contribution. Calculations of the effective number of the Bohr magnetons revealed that the orbital contribution to the magnetic moment comes mainly from the RE^{3+} ions.

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1. Introduction

Molybdates and tungstates containing rare-earth (RE) ions are still attractive as the laser host materials and phosphor-converted white light-emitting diodes (pc-WLEDs) due to a very high stability of light emission, high efficiency, long lifetime and low excitation threshold, safety of work, and environment friendly [1, 2].

Two families of novel polycrystalline copper and rare-earth metal tungstates of the general formula, $Cu_3RE_2W_4O_{18}$, where RE = Sm, Eu, and Gd as well as RE = Dy, Ho, and Er have been successfully obtained and characterised by us using powder X-ray diffraction (XRD), IR, differential thermal analysis-thermogravimetric (DTA-TG) and EPR techniques [3, 4]. Our studies have shown that when RE = Sm–Gd, the $Cu_3RE_2W_4O_{18}$ tungstates crystallize in the triclinic system and show a different type of structure in comparison to the compounds when RE = Dy–Er (the monoclinic system) [4].

Our earlier studies on a novel copper and europium tungstate, $Cu_3Eu_2W_4O_{18}$, have shown that it exhibits a weak temperature dependence of the magnetic susceptibility without a Curie–Weiss region as well as interesting electrical properties, i.e. the thermally activated p-type electrical conduction with the activation energy of 1.11 eV and the large value of relative permittivity $\varepsilon_r \approx 217$ above the room temperature. A larger lossiness ($\delta \approx 9°$) for this tungstate is visible at 10^{-1} Hz and above the room temperature and which may be caused with electrical conduction (losses of Joule–Lenz) [5].

This paper presents the magnetic properties of $Cu_3RE_2W_4O_{18}$ tungstates for RE=Gd, Dy–Er, that differ essentially to those for $Cu_3Eu_2W_4O_{18}$ [5] while the electrical properties should be similar.

2. Experimental details

Copper tungstate ($CuWO_4$) and an adequate rare-earth metal tungstates (RE_2WO_6) were used as the starting materials for a high-temperature solid state synthesis of $Cu_3RE_2W_4O_{18}$ compounds (RE = Gd, Dy–Er) [3, 4].

Dynamic (ac) magnetic susceptibility was measured with the aid of a Quantum Design System (MPMS XL) and recorded in the temperature range 4.2–300 K and at an internal oscillating magnetic field $H_{ac} = 3.9$ Oe with an internal frequency $f = 300$ Hz. Magnetization isotherm was measured at 4.2 K in the static (dc) magnetic field up to 70 kOe. Both susceptibility and magnetization were measured in the zero-field-cooled mode. A diamagnetic contribution has been taken into account [6] by adding a temperature independent contribution of magnetic susceptibility (χ_0'), and the temperature interval of the Curie–Weiss region has been refined with the aid of the Pearson correlation coefficient, R, better than 99.93% [7, 8]. The effective magnetic moment was calculated from the equation $\mu_{eff} = 2.83\sqrt{C}$, where C is the Curie constant. Magnetization isotherms were measured at 4.2 K in the static (dc) magnetic field up to 70 kOe.

3. Results and discussion

Magnetic parameters are presented in Table and magnetic measurements are depicted in Figs. 1–4 (susceptibility) and in Fig. 5 (magnetization). These results suggest that the tungstates under study are paramagnets in the temperature range 4.2–300 K visible also in the absence of the energy losses in the curve of the imaginary part of magnetic susceptibility, χ'', since there is no magnetic order. The negative values of the paramagnetic Curie–Weiss temperature, θ, suggest the weak antiferromagnetic interactions below the temperature of 4.2 K.

$Cu_3RE_2W_4O_{18}$ (RE = Gd, Dy–Er) tungstates show positive values of temperature independent contribution of magnetic susceptibility [7, 8]. It may indicate the temperature independent contributions of the orbital and Landau diamagnetism, Pauli and Van Vleck paramag-

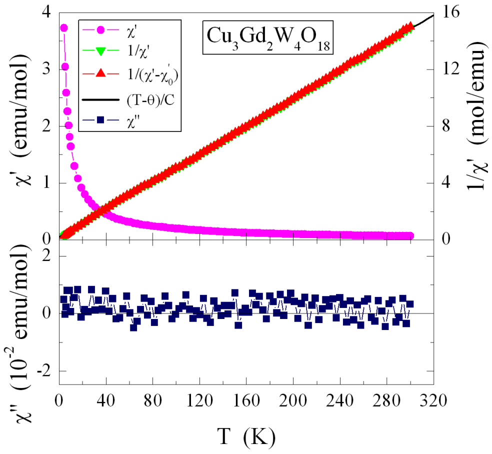

Fig. 1. In phase χ' and $1/\chi'$ as well as out of phase χ'' components of zero field fundamental susceptibility vs. temperature T for $Cu_3Gd_2W_4O_{18}$. The solid (black) line indicates a Curie–Weiss behaviour.

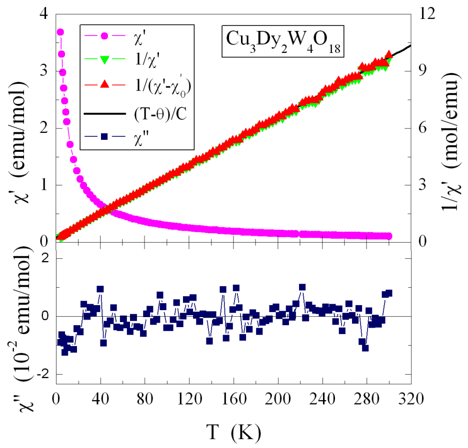

Fig. 2. In phase χ' and $1/\chi'$ as well as out of phase χ'' components of zero field fundamental susceptibility vs. temperature T for $Cu_3Dy_2W_4O_{18}$. The solid (black) line indicates a Curie–Weiss behaviour.

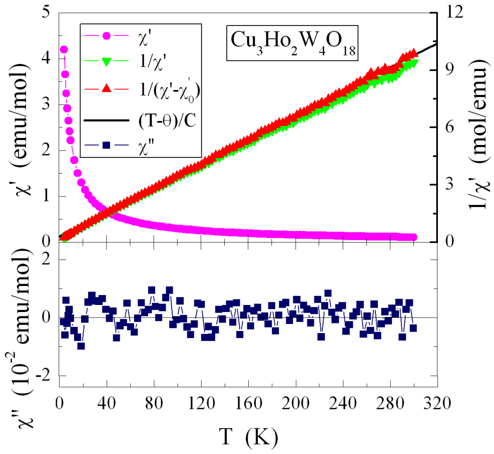

Fig. 3. In phase χ' and $1/\chi'$ as well as out of phase χ'' components of zero field fundamental susceptibility vs. temperature T for $Cu_3Ho_2W_4O_{18}$. The solid (black) line indicates a Curie–Weiss behaviour.

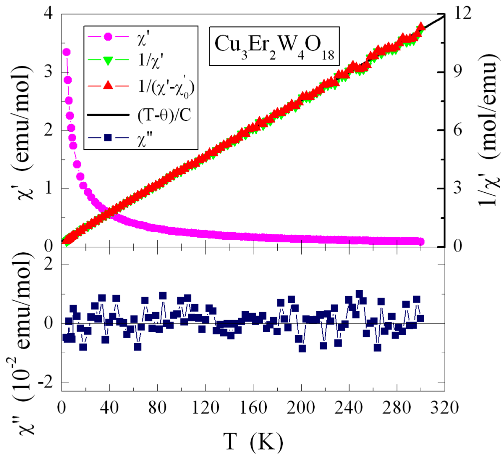

Fig. 4. In phase χ' and $1/\chi'$ as well as out of phase χ'' components of zero field fundamental susceptibility vs. temperature T for $Cu_3Er_2W_4O_{18}$. The solid (black) line indicates a Curie–Weiss behaviour.

TABLE

Magnetic parameters of $Cu_3RE_2W_4O_{18}$ (RE = Gd, Dy–Er). C is the Curie constant, μ_{eff} is the effective magnetic moment, p_{eff} is the effective number of Bohr magnetons, θ is the Curie–Weiss temperature, and χ_0 is the temperature independent contribution of magnetic susceptibility.

RE	C [emu K/mol]	μ_{eff} [μ_B/f.u.]	p_{eff}	θ [K]	χ'_0 [emu/mol]
Gd	20.50	12.81	11.62	−4.4	3.289×10^{-4}
Dy	31.66	15.92	15.35	−7.9	1.522×10^{-3}
Ho	31.62	15.91	15.30	−8.8	4.831×10^{-3}
Er	27.56	14.86	13.88	−8.2	6.454×10^{-4}

netism as well as others, as they cannot be separated. Because the tungstates under study are insulators below 300 K [5], the Landau and Pauli contributions can be neglected and the Van Vleck paramagnetism seems to be a dominating contribution.

The effective magnetic moment well correlates with the effective number of the Bohr magnetons that is the vector sum of effective numbers of RE^{3+} and Cu^{2+} ions. This quantity was calculated from the equation: $p_{eff} = \sqrt{2p^2_{RE^{3+}} + 3p^2_{Cu^{2+}}}$, where $p = g\sqrt{J(J+1)}$, g is the Landé factor taken from Ref. [6] and J is defined as a sum of an effective angular momentum of RE^{3+} ions and the effective spin of Cu^{2+} ones. The latter results from the fact that the JLS-coupling works for the protected RE $4f$-shell, but not for the unprotected TM $3d$-shell [9].

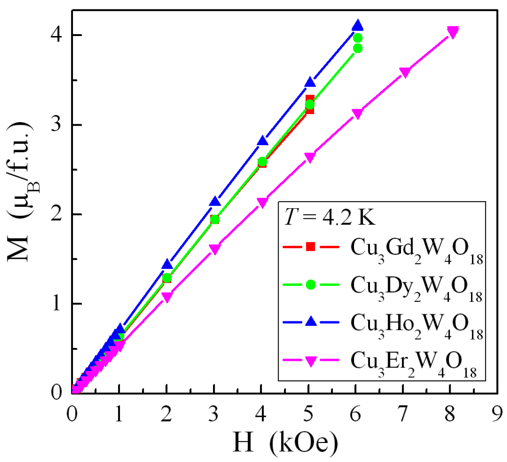

Fig. 5. Magnetization M vs. magnetic field H at 4.2 K for $Cu_3RE_2W_4O_{18}$ (RE = Gd, Dy–Er).

The values of p_{eff} presented in Table show that the orbital contribution to the magnetic moment comes mainly from the RE^{3+} ions.

The magnetic properties of $Cu_3RE_2W_4O_{18}$ tungstates under study are similar to RE_2WO_6 (RE = Nd, Sm, Eu, Gd, Dy, and Ho) [10], $(Co,Zn)RE_4W_3O_{16}$ (RE = Nd, Sm, Eu, Gd, Dy, and Ho) [9], $CdRE_2W_2O_{10}$ (RE = Y, Nd, Sm, Gd–Er) [11], and $MPr_2W_2O_{10}$ (M = Cd, Co, Mn) [12] ones. In all cases above mentioned, the RE^{3+} ions are mainly responsible for the paramagnetic state while the influence of the transition metal (TM) ions on the magnetic properties is slight. The latter strongly influence on the electronic properties because the TM^{3+} ions, as Cu^{2+}, Co^{2+}, Mn^{2+} have both unfilled and unscreened 3*d*-shells [5, 9, 12].

4. Conclusions

$Cu_3RE_2W_4O_{18}$ tungstates under study are the paramagnets with the large orbital contribution of magnetic moment coming from the RE^{3+} ions except for Gd^{3+} ones. The weak antiferromagnetic coupling below 4.2 K can be a result of the competition between the exchange interactions coming from the RE^{3+} and Cu^{2+} ions.

Acknowledgments

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